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# LASER INDUCED REACTION FOR PREBOND SURFACE PREPARATION OF ALUMINIUM ALLOYS

Stage 2 Report (7-10/93)
Contract No. F61708-93-Coo5

by

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## 1. INTRODUCTION

The potential of excimer ArF UV lasers as prebonding treatment technique for Al-2024 alloy adherends was demonstrated in a previous investigation(1) using a room temperature cured modified epoxy adhesive(2).
Surface treatment of the Al adherend by excimer laser causes the removal of weak surface boundary layers, oxidation and morphological changes of the surface.Those surface modifications improve adhesion strength at optimal laser conditions,as expected from theoretical considerations of adhesion mechanisms(mechanical interlocking,physical and chemical bonding,etc.).

The objective of this research is to establish the effect of the various parameters of the excimer ArF UV laser on the Al alloy surface microstructure and chemical activity and to evaluate the correlation between the macro behavior as reflected in shear and peel strength and the microstructure of failure locus of bonded joints. In this phase elevated temperature cured structural adhesives were used.
These adhesives are normally used in bonding and repair process for aerospace application.Surface treatment for bonding Al adherends with these adhesives involve the use of harsh chemicals such as acids bases and organic solvents.Laser surface irradiation can thus be used as an optimal, ecologically favorable treatment. In order to achieve high adhesive strength optimal laser parameters should be found.

The second stage of this research (0002 of the contract) is summarized in this report. The results of this stage present the correlation between the various laser parameters and the adhesive shear strength in order to achieve the maximum shear strength for the structural adhesives specified during the first stage (0001 of the contract). The effect of time interval between laser irradiation and adhesive bonding (open time) is also reported.

# 2. EXPERIMENTAL

## 2.1 Laser Treatment

The laser used during the course of this investigation was a UV excimer ArF (193 nm) laser EMG 201 MSC manufacture by "Lambda Physik", Germany. Beam cross section was 20mmx5mm with energy of 200mj/p*$cm^2$.Higher laser energies were achieved by reducing the laser beam area using focusing lens. Repetition rate was 30Hz and the number of pulses ranged between 1-5000.

Specimen scanning was done by moving the specimen by means of controlled x-y-z table. All experiments were conducted at ambient temperature and room environment. Fig 2.1 shows schematic drawing and photo of the irradiation system.

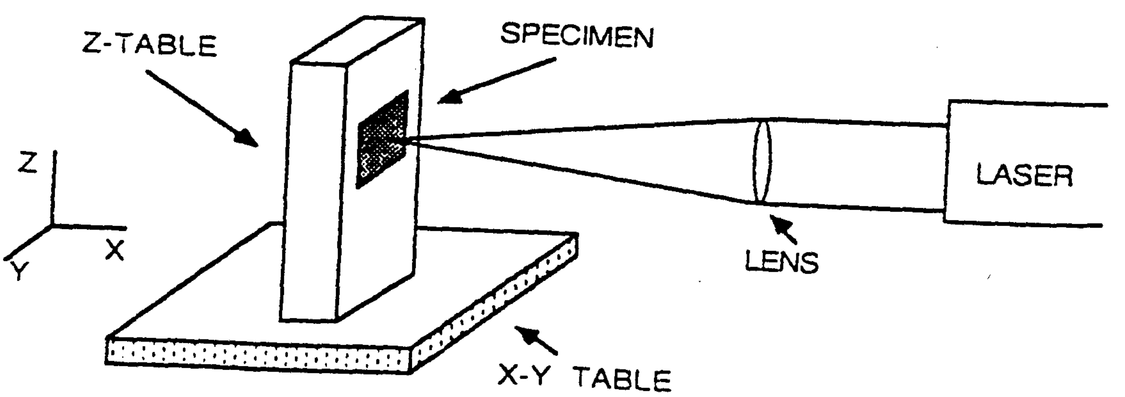



Figure 2.1a: Schematic drawing of irradiation system

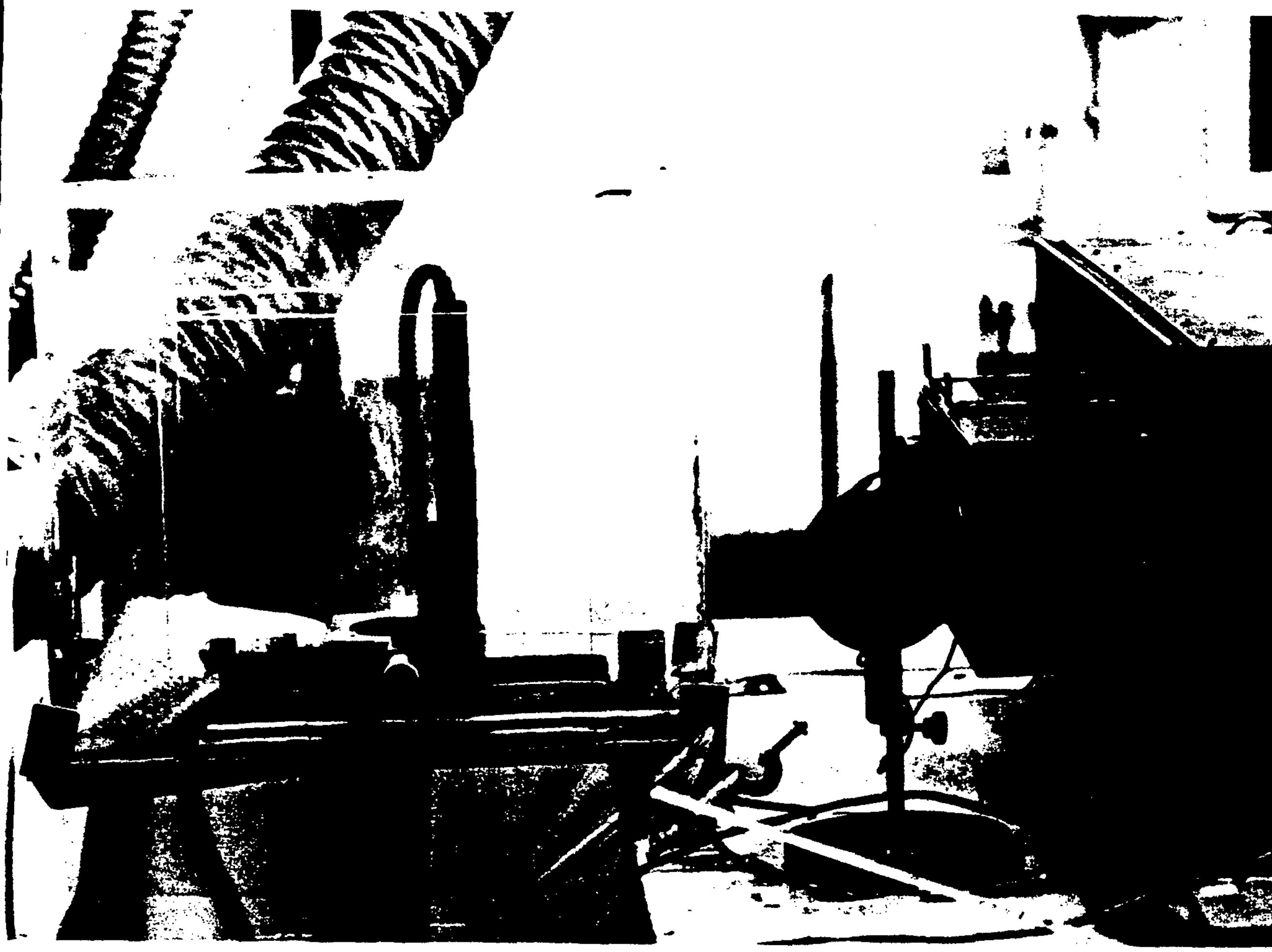


Figure 2.1b: Photograph of irradiation system

## 2.2 Adherend and Adhesives

The adherends used throughout this work are Al 2024-T3. Irradiated specimen are bonded by three different structural adhesives after primer application. Table 2.1 summarizes data of applied adhesives and primers.

**Table 2.1:The structural adhesives and primers**

| ADHESIVE COMMERCIAL NAME (CYANAMID) | CURING CONDITIONS | APPLICATION FORM | SERVICE TEMPERATURE RANGE |
|---|---|---|---|
| FM73 | 1 Hr. 120 $^{o}$C<br>40psi | FILM,0.38mm<br>POLYESTER CARRIER | -55 $^{o}$C to +120 $^{o}$C |
| FM3002K | 1.5Hr. 120 $^{o}$C<br>40psi | FILM,0.3mm<br>POLYESTER CARRIER | -55 $^{o}$C to +175 $^{o}$C |
| FM350NA | 1Hr. 177 $^{o}$C<br>30psi | FILM<br>GLASS CARRIER | -65 $^{o}$C to +177 $^{o}$C |
| BR127 | 1/2Hr. R.T<br>1/2Hr. 121 $^{o}$C | MIXING,BRUSHING | -55 $^{o}$C to +177 $^{o}$C |
| A187 | 1/2Hr. R.T<br>1/2Hr.90 $^{o}$C | BRUSHING<br>2cc A187 in<br>80cc ethanol and<br>20cc D.I. water | - NA - |

## 2.3 Testing

Adhesive joints properties are determined using Single Lap Shear joints (SLS) according to ASTM D-1002-72.The mode of failure is determined to be either adhesive (locus of failure at adhesive/substrate interface) or cohesive (locus of failure in the adhesive matrix).
Surface of irradiated area and fracture surface morphology are studied by Scanning Electron Microscope (SEM) (Jeol model JMS 840, Japan) equipped with Energy Dispersive System (EDS, Link model 290).

## 2.4 Methodology

Two kinds of references are used in all the experiments for comparison with laser treated specimens: a non-treated Al 2024-T3 and unsealed chromic acid anodized Al (according to MIL-A-8625C).The second reference is a conventional pre bonding treatment for aluminum alloy.The shear strength of the reference joints are tested with the same adhesives and primers as the laser treated ones.

Primer application is carried out immediately after laser irradiation.

For optimization three conditions were examined : laser treatment and primer BR127 application, laser treatment and primer A187 application and laser treatment without primer. Usually the adherends are kept in a desiccator between primer application and bonding,except for the investigating of open time for which the adherends were wrapped in paper.

Optimal conditions i.e. 180mj/p*$cm^2$ and 2000 pulses were selected for the open time experiment(1).

Two kinds of "open time" experiments were conducted with laser treatment - with and without primer application.

## 3. RESULTS AND DISCUSSION

### 3.1 Optimization of irradiation conditions for adhesive bonding with structural adhesives. Mechanical SLS Results

Investigation of the effect of prebonding surface treatment with excimer laser on three structural adhesives was carried out. Adhesive bonding joints strength and properties were determine using Single-Lap-Shear joints (SLS).

Tables 3.1-3.5 summarize the optimization experiments with the three adhesives.
Table 3.1 summarizes experiments results with primer BR127 and the three adhesives, table 3.2 summarizes experiments results with primer A187 and adhesive FM73, table 3.3 summarizes experiments results with fresh primer BR127 and adhesive FM73, table 3.4 summarizes experiments' results without primer and adhesive FM73 and table 3.5 summarizes experiments results with primer A187 and three adhesives.

Table 3.1 shows that the highest lap shear strengths for laser treated joints was achieved with FM73 adhesive .The shear strength of laser treated joints was 287Kg/cm$^2$ compared to 429Kg/cm$^2$ of unsealed anodized joints and 128Kg/cm$^2$ of untreated joints .Locus of failure for laser treated joints with FM73 adhesive is cohesive as for anodized joints.
Shear strengths of laser treated joints with adhesives FM3002K and FM350NA and primer BR127 are low(100 and 92Kg/cm$^2$) and about 1/3 of unsealed anodized joints (table 3.1). Locus of failure for laser treated joints is adhesive while for unsealed anodized joints it is cohesive.
It should be noted that BR127 is not the primer advised for FM350 NA. The advised primer BR154 is on its way to our lab. and will be further investigated.

**Table 3.1** :Adhesive shear strength for three structural adhesives - primer BR127.Laser energy 180mj/p*cm$^2$

| SAMPLE | PULSE NO. | ADHESIVE | S.L.S Kg/cm$^2$ | FAILURE MODE |
|---|---|---|---|---|
| UNTREATED | | FM300K | 39.5±3 | a |
| ANODIZED | | | 305.6±25 | m |
| LASER TREATED | 600 | | 88.0±8 | a |
| | 1000 | | 86.8±20 | a |
| | 2000 | | 101.3±15 | a |
| UNTREATED | | FM73 | 127.7±19.4 | c |
| ANODIZED | | | 428.6±5.7 | c |
| LASER TREATED | 600 | | 286.8±16.4 | m |
| | 1000 | | 280.5±15.5 | m |
| | 2000 | | 286.9±4.6 | c |
| UNTREATED | | FM350NA | 55.2±5.3 | a |
| ANODIZED | | | 264.1±15.3 | c |
| LASER TREATED | 600 | | 92±8.7 | a |
| | 1000 | | 86.1±12.5 | a |
| | 2000 | | 77.5±5.5 | a |

c - cohesive failure

a - adhesive failure

m - mixed failure

The unsatisfying results of the laser and BR127 treatment was probably due to the effect of etching of the surface which ruins the fine morphological structure built by the excimer laser treatment.Therefore, another primer was applied based on coupling agents as silane.
A silane A187 was used as a primer for the above adhesives. The advantages of A187 are: homogeneity and water base (no etching of anodization). This primer may react chemically with the aluminum oxide of the adherend and the epoxide group of the adhesive through its end groups(3).

Table 3.2 summarizes the shear strengths of the laser treated joints with the adhesive FM73 and A187 as a primer. The results show improved shear strengths with A187 ($334 Kg/cm^2$) compared to those for BR127 ($289 Kg/cm^2$). Unsealed anodized joints have shear strengths of $394 Kg/cm^2$. Untreated joints have also high shear strength ($303 Kg/cm^2$) due to silane effect.
Experiments with a fresh BR127 primer and an adhesive FM73 (table 3.3) show that laser treated joints have shear strength similar to those with a primer A187 ($329 Kg/cm^2$). Experiments without a primer (table 3.4) and with an adhesive FM73 show shear strength of $321 Kg/cm^2$.
Failure mode of laser treated joints is cohesive for all the experiments summarized in tables 3.2-3.4.

**Table 3.2:** Adhesive bonding shear strength - adhesive FM73, primer A187- with and without oxygen during laser irradiation. Laser energy 180mj/p*cm$^2$.

| SAMPLE | PULSE NO. | ADHESIVE | S.L.S Kg/cm$^2$ | FAILURE MODE | |
|---|---|---|---|---|---|
| UNTREATED | | FM73 | 303.4±6.4 | c | |
| ANODIZED | | | 393.9±18 | c | |
| LASER TREATED | 100 | | 301.4±1.7 | c | WITHOUT OXYGEN |
| | 600 | | 316±15.8 | c | |
| | 1000 | | 334±10.7 | c | |
| | 2000 | | 319±9.6 | c | |
| LASER TREATED | 100 | | 310.7 | c | WITH OXYGEN |
| | 600 | | 298.4±2.2 | c | |
| | 2000 | | 298±7.6 | c | |

c - cohesive failure

a - adhesive failure

m - mixed failure

**Table 3.3:** Adhesive bonding shear strength -adhesive FM73, primer fresh BR127.

| SAMPLE | PULSE NO. | ADHESIVE | S.L.S $Kg/cm^2$ | FAILURE MODE |
|---|---|---|---|---|
| UNTREATED | | FM73 | 127.7±9.4 | c |
| ANODIZED | | | 428.6±1.7 | c |
| LASER TREATED | 1000 $180mj/p*cm^2$ | | 329.6±12 | c |
| | 100 $1J/p*cm^2$ | | 312±29 | |

c - cohesive failure
a - adhesive failure
m - mixed failure

**Table 3.4:** Adhesive bonding shear strength -adhesive FM73, without primer.Laser energy $180mj/p*cm^2$.

| SAMPLE | PULSE NO. | ADHESIVE | S.L.S $Kg/cm^2$ | FAILURE MODE |
|---|---|---|---|---|
| ANODIZED | -- | FM73 | 370±7.7 | c |
| LASER TREATED | 600 | FM73 | 302±15 | c |
| | 1000 | | 302±14 | c |
| | 2000 | | 321±4.5 | c |

c - cohesive failure

Table 3.5 summarizes the shear strengths for the three adhesives with the primer A187. Higher shear strengths are achieved for laser treated joints in comparison to results with primer BR127 ( table 3.1).

Figure 3.1 shows the failure modes for this experiment.

Best results are reached for the adhesive FM73 possibly due to its better compatibility with the primer A187. Highest shear strengths for laser treated joints are $344Kg/cm^2$ (table 3.5 ) compared to unsealed chromic anodized joints with $398Kg/cm^2$.The cohesive mode of failure is shown clearly in fig.3.1a.

Shear strengths of laser treated joints with adhesives FM350NA and FM300 2K and primer A187 reached values of $217Kg/cm^2$ and $294Kg/cm^2$,respectively(table 3.5).

Locus of failure for laser treated joints is cohesive with FM300 2K and is adhesive with FM350NA(FIG.3.1B).For the adhesive FM350NA another primer will be applied(BR154).

The shear strength of unsealed chromic anodized joints is $249Kg/cm^2$ for the adhesive FM350NA with primer A187(table 3.5),and the shear strength of the anodized joints for FM3002K and primer BR127 is $304Kg/cm^2$ (table 3.1).These values of shear strength are close to the values of the shear strength of laser treated joints(table 3.5).

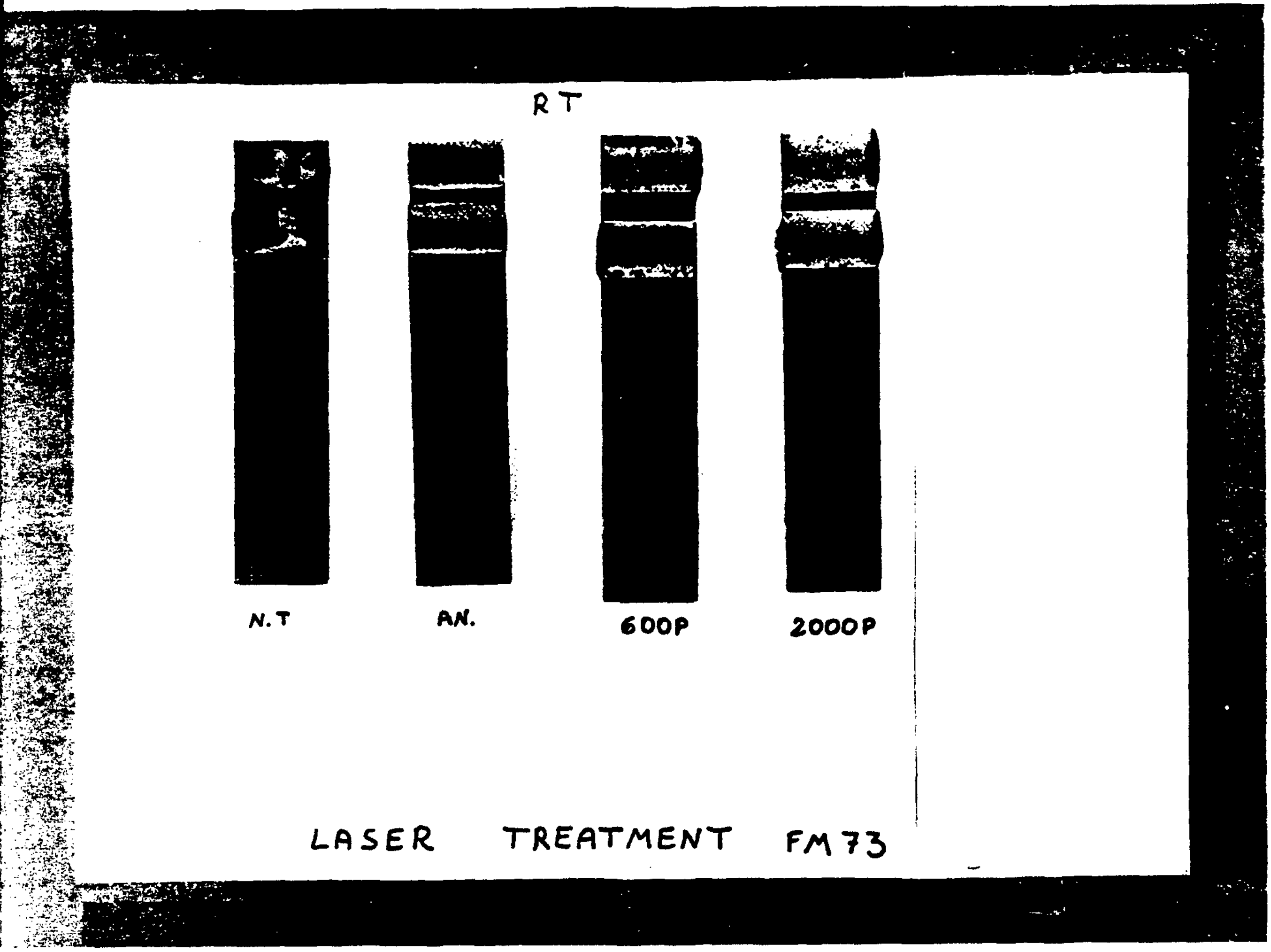
**Table** 3.5: Adhesive bonding shear strength for three structural adhesives primer A187. Laser energy $180 mj/p*cm^2$

| ADHESIVE | FM73 | FM3002K | FM350NA |
|---|---|---|---|
| SAMPLE | S.L.S $Kg/cm^2$ | S.L.S $Kg/cm^2$ | S.L.S $Kg/cm^2$ |
| UNTREATED | 303.4±6.4(C) | | 103±3(A) |
| ANODIZED | 393.9±18(C) | | 249±17(A) |
| LASER TREATED | | | |
| 1000 PULSES | 325.7±28(C) | 294.5±7(C) | 217±29(A) |
| 2000 PULSES | 344.3±12.8(C) | 207±30(C) | 190±5(A) |
| 5000 PULSES | 330.5±13(C) | 289±32(C) | 182±28(A) |

c - cohesive failure

a - adhesive failure

m - mixed failure



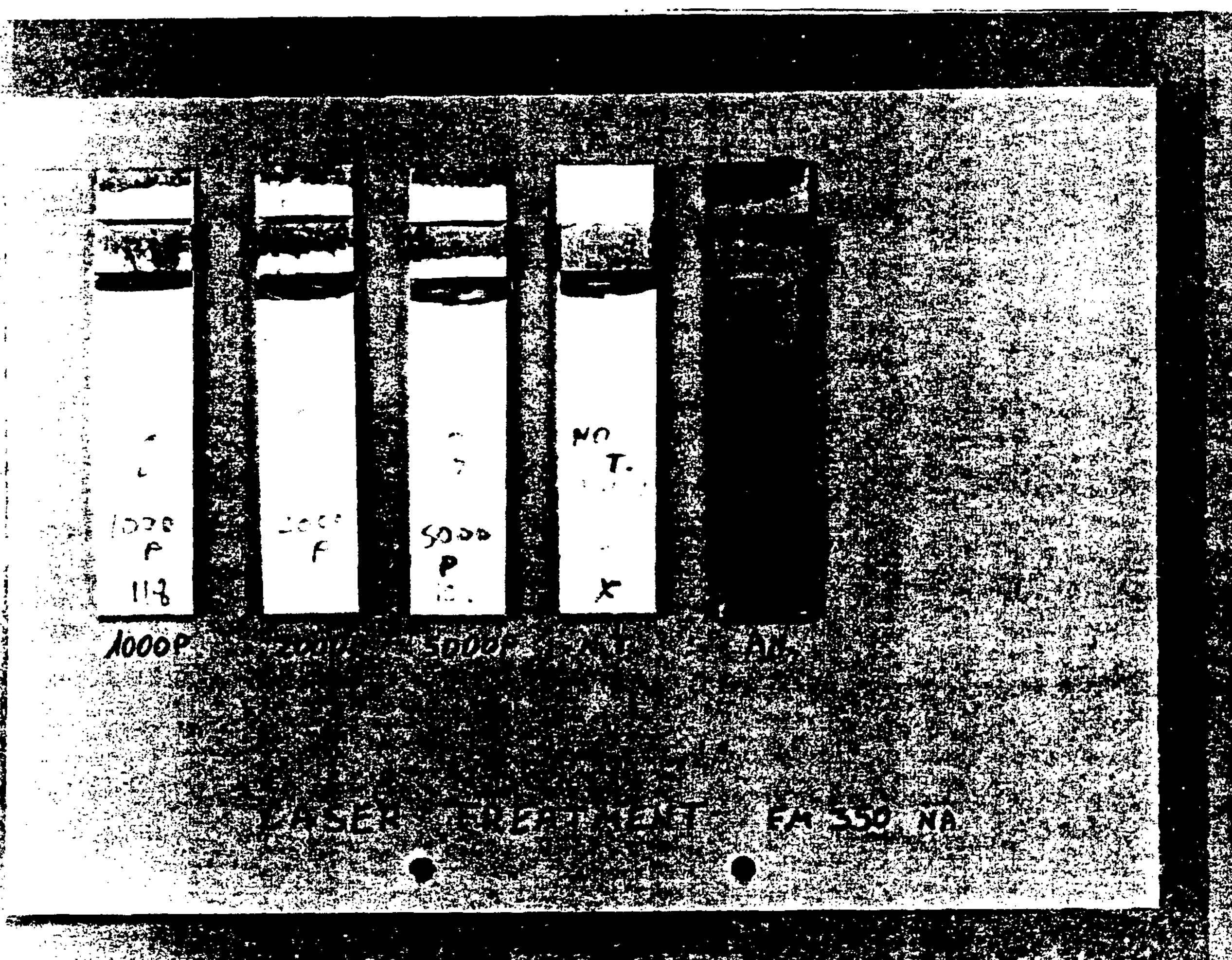




Figure 3.1:View of failure mode for a:adhesive FM73 and primer A187 , b: adhesive FM350NA and primer A187.

### 3.2: <u>Effect of "Open time" between Irradiation and Adhesive Bonding.</u>

The effect of "open time" between laser irradiation treatment and bonding is summarized in table 3.6. Fig.3.2 shows the failure mode of the joints after SLS tests.
Table 3.6 and fig.3.3 indicate that there is a slight decrease in shear strength as open time intervals increase, but no significant change is observed even after 20 days of open time.
Primer application directly after laser irradiation improves the adherends treatment durability (higher shear stress and less degradation).
Fig.3.2 shows the cohesive failure mode after SLS tests.

Table 3.6 : **Effect of Interval Period between Irradiation and Adhesive Bonding.** (Adhesive FM73,laser energy 180mj/p*cm$^2$,2000pulses.)

| SAMPLE<br><br>OPEN TIME<br>days | PRIMER A187<br>SLS<br><br>Kg/cm$^2$ | WITHOUT PRIMER<br>SLS<br><br>Kg/cm2 |
|---|---|---|
| 1 | 328±13 (c) | 275±12 (70%c) |
| 3 | 344±13 (c) | 321±5 (70%c) |
| 4 | 322±4 (c) | 300±9 (70%c) |
| 10 | 303±3 (c) | 302±17 (70%c) |
| 15 | 321±12 (c) | 296±3 (80%c) |
| 20 | 306±6 (80%c) | 266±14 (60%c) |

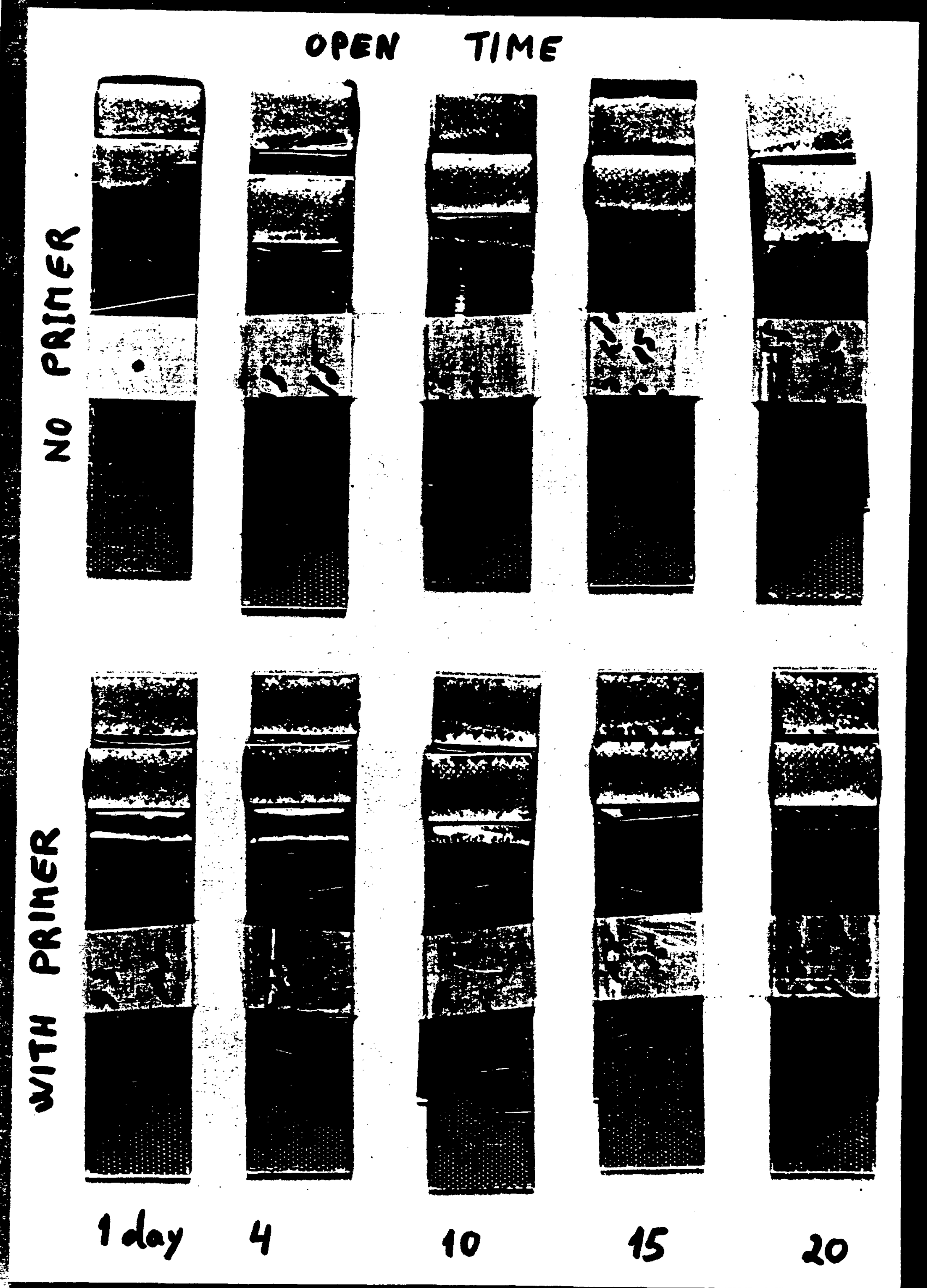



Figure 3.2:View of laser treated joints after SLS tests -bonding after varius time interval.

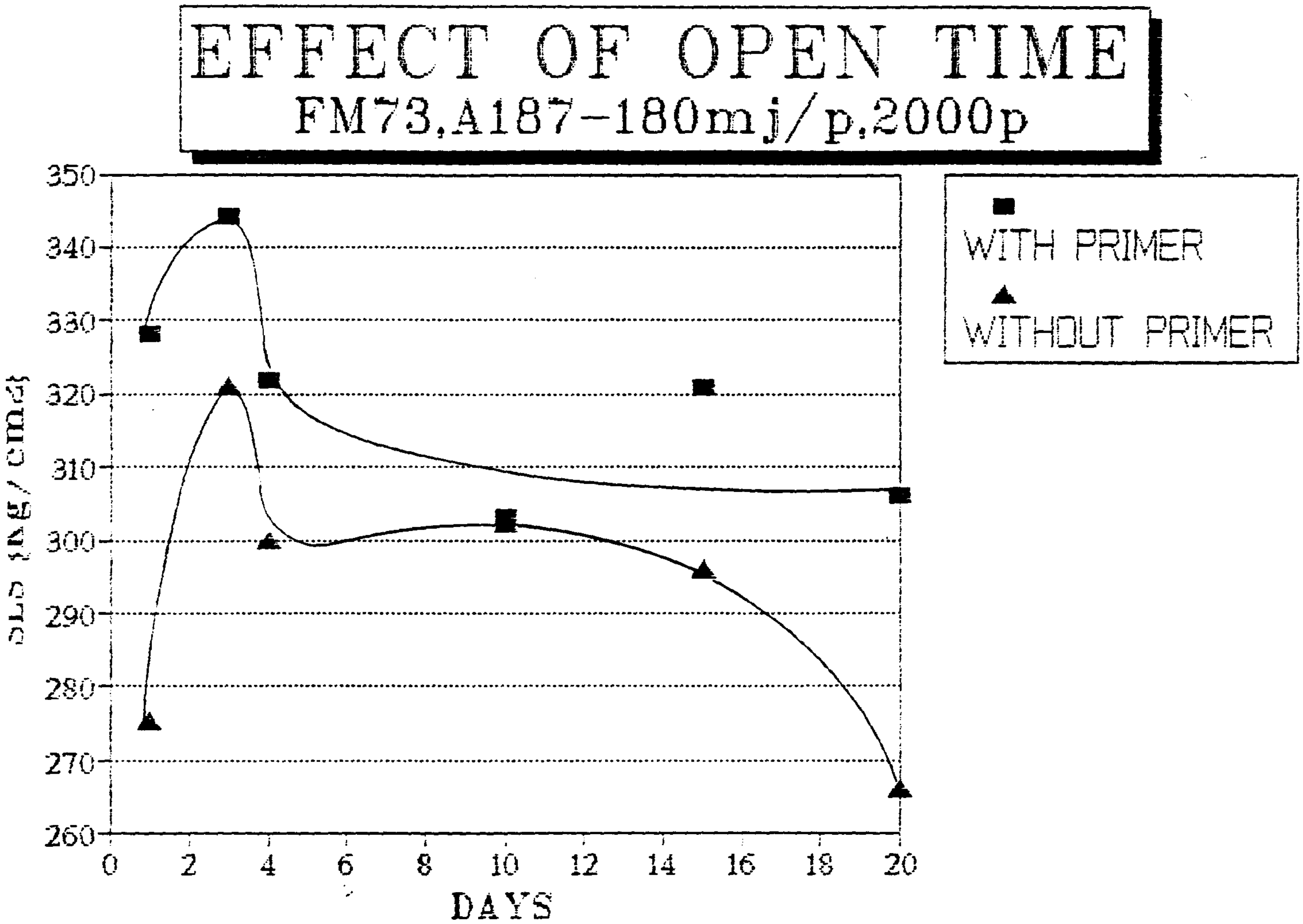



Figure 3.3: Adhesive strength after optimal laser treatment at various periods of "open time".

## 4. Conclusions

Laser treatment improved the shear strength of bare Al adherends by 300% but shear values are still lower than those of chromic anodization treated adherends.

Applying a primer BR127 did not improve the shear strength probably due to etching of the fine morphology created by the laser treatment on the surface of the adherend.

Silane A187 is suitable as a primer following laser irradiation for two of the three adhesives(FM73 and FM300 2K).

The advantages of A187 are: homogeneity and water base (no etching of anodization).This primer may react chemically with the aluminum oxide of the adherend and the epoxide group of the adhesive through its end groups(3). A187 is a water based primer which does not contain acids or chromate particles as in the case of BR127 thus being ecological favorable .

The values of shear strength after laser treatment of Al 2024 adherends, application of the primer A187, and using the adhesives FM73,FM300 2K are similar to those of unsealed anodization treatment and are high enough to be suited for structural bonding.The highest values that were achieved are 344Kg/cm$^2$ with FM73 and 294Kg/cm$^2$ with FM300 2K, compared to those of the anodized adherends (394Kg/cm$^2$ and 306Kg/cm$^2$,respectively).

Adhesive bonding can be applied even 20 days after laser treatment providing that primer is applied immediately after laser irradiation.

Adhesion with FM350 NA should further be improved.

**REFERENCES**

1.H.Dodiuk, A.Buchman, S.Kenig, M.Rotel, J.Zahavi, T.J.Reinhart: J.Adhesion, vol.41,1993, pp.93-112.

2.H.Dodiuk, U.S.Patent No.4841010, June 20,1989.

3.E.Plueddmann, Poly. Mat. Sci.,24, pp. 493 ,1984.